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Process Analysis and Modelling for 2nd Generation Lignocellulosic Bioethanol Production

Giacomo Filippo Porzio, Matteo Prussi, David Chiaramonti*

CREAR, c/o Dept. of Energetics "S.Stecco", University of Florence, 50139, Florence, Italy. david.chiaramonti@unifi.it

In the present work, the most promising processing technologies for next generation ethanol production are assessed. A literature-based comparative analysis of the technologies in terms of yield, efficiency, feedstock and level of process integration is carried out in order to identify the most interesting ones. The aim of this paper is the analysis and validation based on literature data of a process simulation performed using the software Aspen Plus®. The model is intended to understand the major process steps and focuses on the main aspects from an energy engineering point of view. Moreover it provides an useful tool for preliminary analysis of different configurations. Crucial aspects include high pretreatment yield, efficient hexose and pentose fermentation, enzyme strain development and solid residue valorization for process heat and power generation. Energy and mass balances are modeled, so to allow a comparison among different technological solutions. A plant able to process 240,000 kt/y of biomass is modeled, showing a production capacity of about 40,000 kt/y of ethanol. Ethanol productivity is over 300 L/t of dry biomass, and net process energy efficiency is calculated over 35%. The model developed focuses on the main steps of the production process allowing for further development or process optimization.

1. Introduction

The international attention focuses more and more on developing sustainable alternatives to fossil fuels, given the steady increase in oil prices and its reserves' announced diminution. Renewable sources of energy, and particularly biofuels are a promising option to ensure energy security in the future, resulting in simultaneous economic and environmental benefits. To promote the diffusion of biofuels, the European Union laid down ambitious targets for their utilization, establishing a minimum market penetration percentage of 5.75% by 2010 and 10% by 2020. One such biofuel is bioethanol. Biomasses for fuel production can generally be divided into two categories, organic wastes and dedicated energy crops. A further division includes starch or sugar crops and ligno-cellulosic biomass (Fig.1), the former feedstock referred to the production of "first generation" bioethanol and the latter of "second", or "next generation" one. The production of ethanol from sugary and starchy biomasses is a well-known process, and only few improvements are possible from the technical, sustainability and economical point of view. Most of the cultures dedicated to the production of first generation bioethanol are potential food crops such as cereals (mostly corn) and sugar beet or sugar cane (Chiaramonti, 2007; and Sassner et al.,

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2007). The process followed for the production of first generation bioethanol (C_2H_5OH) is sugar extraction from the plants (or from starch via hydrolysis) and its fermentation. Hydrolysis of starch is an established technology, using enzyme cultures to produce glucose. The fermentation is achieved by the action of fungi, bacteria or yeasts in absence of oxygen (Mosier et al., 2005, Hahn-Hägerdal et al., 2006). The main co-products of such a process are Distillers Dried Grains with Solubles (DDGS) and CO_2. Theoretical yields are 0.568 kg ethanol/kg starch, and 0.538 kg ethanol/kg saccharose (Chiaramonti, 2007; and Mustafa et al., 2007). The research is currently also investigating the opportunity of utilizing bacteria for the fermentation, which seem able to perform fermentation in shorter times than yeast (Hamelinck et al., 2005; Hahn-Hägerdal et al., 2006, Chiaramonti, 2007). Second generation bioethanol processing requires the operation of some pretreatment techniques to break the biomass fibre structure, making cellulose and hemicellulose more accessible to enzymes that convert carbohydrates into sugars, thus allowing the subsequent fermentation steps to occur (Mosier et al., 2005). Among pretreatment techniques, which usually vary according to the type of feedstock used, the most promising are: uncatalyzed steam explosion, liquid hot water (LHW), acid/alkali pretreatment, Ammonia fiber explosion (AFEX) (Mosier et al., 2005, and Hahn-Hägerdal et al., 2006). An acid or enzymatic hydrolysis treatment of the pre-treated biomass is usually carried out to release sugars for the subsequent fermentation and enhance the final process conversion rate. Fermentation can either be done by a single microbial culture, able to digest all the sugars of the hydrolysis broth, or by utilizing different organisms in a multi-step process with separate optimization of every conversion step (Hamelinck and Faaij, 2006). Sassner et al. (2007) reported that a process based on enzymatic hydrolysis and fermentation is regarded as the most promising alternative in the conversion of carbohydrates from lignocellulosic materials into ethanol in an energy-efficient way with high yields and low production cost. This is reflected by the demo plants that have been or are under development, mostly based on enzymatic hydrolysis. Despite the complexity of these process steps, they offer significant advantages compared to first generation biofuels. This is the reason why second (or, in a wider sense, “new generation”) biofuels represent a key element in EU renewable strategy.

2. Materials And Methods

Pilot-scale plants and demonstration facilities have recently been starting operation in several places world-wide (NREL and Abengoa Bioenergy Corp, USA and Spain; Iogen Corp, Canada; SEKAB, Sweden; Souston, France; M&G-Chemtex, Italy). These processes vary for feedstock chosen, level of implementation, operating conditions, level of process integration, yields and production technology. Each one has different advantages and disadvantages; however, process concepts have not yet been demonstrated on industrial scale (Hahn-Hägerdal et al., 2006, and Sassner et al., 2007). Analysis and comparison of these processes has allowed to identify as one of the most promising conversion technologies a process in which steam explosion with mild acid as catalyst and SSCF with enzymatic hydrolysis are performed, using poplar as feedstock. A computer model of the selected process has been carried out as final step

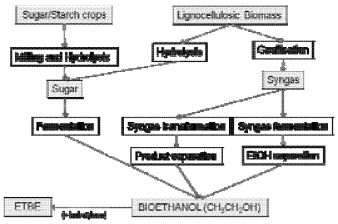

Figure 1: Main bioethanol production patways (Chiaramonti, 2007).

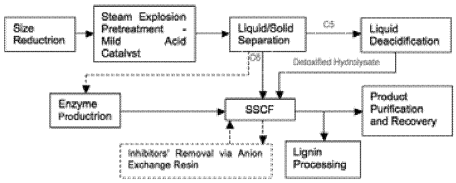

Figure 2: Simulated process Block Flow Diagram.

of the analysis using Aspen Plus® (Fig. 2), taking as a reference analogous simulations from NREL (Aden et al., 2002; and Wooley et al., 1999). Additional components have been added where necessary together with physical properties. The model developed consists of five main blocks, which identify separate phases, or steps, of the process. These are, in order:

- Pretreatment,
- SSCF,
- Enzyme Production,
- Product Distillation and Purification,
- Steam and electric energy generation.

A process with mild acid catalyzed two-steps steam explosion pretreatment, and Simultaneous Saccharification and Co-Fermentation (SSCF) is simulated. In the model, two step dilute acid steam explosion (4.4 and 13.2 bar) is analyzed, releasing 80% of the available pentoses which are directly sent to the fermentation step. The addition of mild acid was found to enhance the yield allowing a moderate formation of fermentation inhibitors, which are removed through neutralisation and an ion-exchange membrane resin. The following step of the process is SSCF, carried out in a single reactor, in which enzymes and yeast are added. Conversion rate of cellulose to glucose is set to 89.2%; C6 and C5 sugars to ethanol rates are respectively 92% and 85% (Wooley et al., 1999). The utilisation of a small number of reactors is beneficial in terms of investment costs, and as process integration evolves towards consolidate bio-processing the biological cultures become more and more relevant, especially their adaptability to different temperatures (Goršek and Zajšek, 2010). In the model two options are considered concerning enzyme production: to produce the required strain in the facility, deducing part of the pretreated slurry to feed microbial cultures and to purchase all the microorganisms required for the process. Product separation is the most energy-intensive block of the simulation after pretreatment, requiring a two-stage distillation and a vapor molecular sieve for ethanol dehydration. One of the most interesting parts of the model is the utilities section where the valorisation (burning) of the lignin-rich solid residue allows the production of superheated steam to cover the process thermal energy needs. Steam evolves through a multistage steam turbine producing an extra electric power output. The process environmental balance is even more positive if the valorisation of other side products is considered. Particularly interesting is the option of CO_2 capture and storage performed through the insertion of a

four stage-intercooled compression to 110 bar at the gas scrubber outlet. This operation requires a considerable amount of energy and reduces the overall process efficiency, but advantages may derive from the obtaining of CO_2 emission allowances. 4.3 t of CO_2/h can be removed and stored. In any case the overall carbon dioxide balance is negative, since no traditional fuel is required to run the process and all the carbon emitted for burning was first absorbed by the plant during its growth.

3. Results

The base case simulation results in an ethanol production of 4,792 kg /h of Ethanol, which means 38.34 kt/y with a biomass feed of 240,000 t/y on a wet basis. The ratio between liter of ethanol production and tons of dry biomass is therefore 303.3. Better results are achieved in the enzyme purchasing option, since both ethanol flowrate and productivity are increased. Table 1 compares the results of the simulated process – both with and without enzyme production – to literature results. Considering a LHV of 19,384 kJ/kg for poplar and 26,709 for ethanol, about 108 MW of biomass produce 36 MW of ethanol and 2.5 MW of net electric power, resulting in a process energy efficiency of 35%, expressed as:

$$\eta_{conv} = \frac{ethanol\_Heating\_Value\_[MW] + electric\_power\_output\_[MW]}{biomass\_Heating\_Value\_[MW]}. \quad (1)$$

Table 2 summarises the energy uses of the process, compared to analogous literature simulations (Sassner et al., 2008; and Piccolo and Bezzo, 2009). As expected, the enzyme purchasing option corresponds to higher production, which is increased by a 4.3%, and the overall EtOH productivity reaches 316 L/t dry biomass. Energy production is higher (thanks to the increase in the combustor feed flow) and power consumption lower since no power has to be supplied to the enzyme section, resulting in an increase in process energy efficiency.

Table 1: Process main results compared to similar processes in literature.

	Base case	Enzyme purchasing	Sassner et al., 2008			Piccolo and Bezzo, 2009
Biomass	Poplar	Poplar	Salix	Corn Stover	Spruce	Wet hardwood chips
Process feed (kt/y)	240,000	240,000	200,000			700,000
Ethanol Product Flowrate (kg/h)	4,792	4,999				20,864
Ethanol productivity (L/t dry biomass)	303	316	314	306	315	312

Table 2: Process energy results compared to literature.

	Base case	Enzyme purchasing	Sassner et al., 2008			Piccolo and Bezzo, 2009
Biomass[a]	[1]	[1]	[2]	[3]	[4]	[5]
Biomass HV (MW)	107.7	107.7				
Ethanol HV (MW)	35.56	37.08				156
Electric power (MW)	2.43	2.78				5.9
η_{conv}	35%	37%	33%	34%	33%	39%

[a][1] for Poplar, [2] for Salix, [3] for Corn Stover, [4] for Spruce, [5] for Wet hardwood chips.

The estimated total process energy requirement is 18.32 MJ/L EtOH. A comparison of the total process requirements with literature is reported in Table 3.

Table 3: Total process energy requirements compared to literature (MJ/L ethanol).

Stage	Our simulation	Piccolo and Bezzo, 2009	Sassner et al., 2008	Cardona and Sànchez, 2006	Lynd, 1996	Hamelinck et al., 2005
Pretreatment	13.25	4.69		4.23	2.46	2.46
Distillation	5.01	2.39		27.89	5	5
Dehydration	0.07	1.11				
Evaporation		4.34		4.35		
Total	18.32	12.53	14.6-15.9[a]	36.47		

[a]14.6 for Corn Stover, 15.1 for Spruce and 15.9 for Salix.

4. Conclusions

The present paper reported a description of an Aspen Plus® next generation ethanol production process simulation. Based on the comparison of different process options, a process was selected for simulation. Model results have been validated by comparison with analogous process simulations found in literature. The investigated plant size is able to process 240,000 kt /y of biomass, with a production capacity of about 40,000 kt/y of ethanol. Ethanol productivity ranges between 303 and 316 L/t dry biomass; net process energy efficiency is calculated in the range from 35 % to 37 % depending upon different process configurations. The modeling contributed to achieve a better understanding of the production process from a particular feedstock and could be applied as a tool for further research and development on by-products valorization.

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